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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 18/76, 18/48	A1	(11) International Publication Number: WO 98/00450 (43) International Publication Date: 8 January 1998 (08.01.98)
<p>(21) International Application Number: PCT/EP97/02853</p> <p>(22) International Filing Date: 2 June 1997 (02.06.97)</p> <p>(30) Priority Data: 96110378.5 27 June 1996 (27.06.96) EP</p> <p>(34) Countries for which the regional or international application was filed: DE et al.</p> <p>(71) Applicant: IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB).</p> <p>(72) Inventor: BLEYS, Gerhard, Jozef; Bremstraat 19, B-3001 Heverlee (BE).</p> <p>(74) Agents: BAKEN, Philippus, Johannes, Leonardus, Henricus et al.; ICI Europe Ltd., ICI Polyurethanes, Intellectual Property Dept., Everslaan 45, B-3078 Everberg (BE).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: MICROCELLULAR ELASTOMERIC POLYURETHANE FOAMS</p> <p>(57) Abstract</p> <p>A method for the preparation of microcellular elastomeric polyurethane foams from a reaction mixture comprising a polyisocyanate component containing at least 85 % by weight of 4,4'-diphenylmethane diisocyanate or a variant thereof, a polyol composition comprising at least one polyoxyalkylene polyol having an average nominal hydroxyl functionality of from 2 to 6, an average hydroxyl equivalent weight of at least 1300 and an average oxyethylene content of between 50 and 85 % by weight, water, a chain extender having an average hydroxyl equivalent weight of from 15 to 250 and optionally a crosslinking agent, the hardblock-content being more than 45 % by weight.</p>		

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TITLE: MICROCELLULAR ELASTOMERIC POLYURETHANE FOAMS**DESCRIPTION**

The present invention relates to the preparation of microcellular elastomeric polyurethane foams.

Conventional polyurethane elastomers are made from formulations which have a
5 hardblock-content of about 30 to 40% by weight (hardblock-content being defined
herein as the sum of the amounts of polyisocyanates, chain extenders and, optionally,
cross-linking agents, relative to the total amount of polymer in weight percent).

Formulations having a higher hardblock-content are difficult to process and result in
10 products with a very high hardness.

Formulations comprising high amounts of 4,4'-MDI and polyether polyols having high
EO-contents have already been used to prepare flexible polyurethane foams, see for
example EP-A 547764, EP-A 547765 and EP-A 549120.

15 The preparation of elastomeric polyurethanes from polyether polyol having low ethylene
oxide (EO)-content is also known, see for example US-A 5122548 and EP-A 13487.

It has now surprisingly been found possible to produce microcellular polyurethane
20 elastomeric foams which have a very high hardblock-content, without having an
excessively high hardness and which are easily processable over a wide density range.

Thus, according to the invention, there is provided a method for the preparation of
microcellular elastomeric polyurethane foams from a reaction mixture comprising a
25 polyisocyanate component, a polyol composition, a chain extender, water and optionally
a cross-linking agent, wherein the polyisocyanate component contains at least 85% by
weight of 4,4'-diphenylmethane diisocyanate or a variant thereof, the polyol composition
comprises at least one polyoxyalkylene polyol containing oxyethylene residues, said
polyol composition having an average nominal hydroxyl functionality of from 2 to 6, an
30 average hydroxyl equivalent weight of at least 1300 and an average oxyethylene content
of between 50 and 85% by weight, and the chain extender has an average hydroxyl

equivalent weight of from 15 to 250, the hardblock-content being more than 45% by weight.

5 The polyisocyanate component used in the method of the invention may consist essentially of pure 4,4'-diphenylmethane diisocyanate or mixtures of that diisocyanate with one or more other organic polyisocyanates, especially other diphenylmethane diisocyanate isomers, for example the 2,4'-isomer optionally in conjunction with the 2,2'-isomer. The polyisocyanate component may also be an MDI variant derived from a polyisocyanate composition containing at least 85% by weight of 4,4'-diphenylmethane diisocyanate. MDI variants are well known in the art and, for use in accordance with the invention, particularly include liquid products obtained by introducing uretonimine and/or carbodiimide groups into said polyisocyanate composition and/or by reacting with one or more polyols.

15 Preferred as the polyisocyanate component are polyisocyanate compositions containing at least 90% by weight of 4,4'-diphenylmethane diisocyanate. Polyisocyanate compositions containing at least 95% by weight of 4,4'-diphenylmethane diisocyanate are most preferred.

20 The term "average nominal hydroxyl functionality" is used herein to indicate the average functionality (number of hydroxyl groups per molecule) of the polyol composition on the assumption that the average functionality of the polyoxyalkylene polyols present therein is identical with the average functionality (number of active hydrogen atoms per molecule) of the initiator(s) used in their preparation although in practice it will often be somewhat less because of some terminal unsaturation. It is preferred that the average nominal hydroxyl functionality of the polyol composition is from 2 to 4, most preferred polyoxyalkylene polyols being diols or triols.

30 The composition may comprise a single polyoxyalkylene polyol which preferably is a poly(oxyethylene-oxypropylene) polyol having the required average nominal hydroxyl functionality, hydroxyl equivalent weight and oxyethylene content. Such polyols are known in the art and may be obtained in conventional manner by reacting ethylene and propylene oxides simultaneously and/or sequentially in any order with an initiator having from 2 to 6 active hydrogen atoms such as water, a polyol, a hydroxylamine or

a polyamine and the like. Examples of polyol initiators are ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,3-propane diol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, glycerin, trimethylol propane, erythritol, xylitol, glucose, fructose, mannitol or sorbitol.

Alternatively, the polyol composition may comprise a mixture of two or more polyols such that the total composition has the required average nominal hydroxyl functionality, average hydroxyl equivalent weight and oxyethylene content. The other polyols may be selected from polyethers, polyesters, polythioethers, polycarbonates, polyacetals, polyolefins or polysiloxanes.

Polyether polyols may be, for example, polyoxypropylene polyols, polyoxyethylene polyols or poly(oxyethylene-oxypropylene) polyols containing less than 50% or more than 85% by weight of oxyethylene residues.

Polyester polyols which may be used include hydroxyl-terminated reaction products of dihydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol or cyclohexane dimethanol or mixtures of such dihydric alcohols, and dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate or mixtures thereof.

Polyesteramides may be obtained by the inclusion of aminoalcohols such as ethanolamine in polyesterification mixtures.

Polythioether polyols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, alkylene oxides, dicarboxylic acids, formaldehyde, amino-alcohols or aminocarboxylic acids.

Polycarbonate polyols which may be used include products obtained by reacting diols such as 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol diethylene glycol or tetraethylene glycol with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

Polyacetal polyols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetals may also be prepared by polymerising cyclic acetals.

5 Suitable polyolefin polyols include hydroxy-terminated butadiene homo- and copolymers and suitable polysiloxane polyols include polydimethylsiloxane diols.

10 Other polyols which may be used comprise dispersions or solutions of addition or condensation polymers in polyols of the types described above. Such modified polyols, often referred to as "polymer" polyols have been fully described in the prior art and include products obtained by the in situ polymerisation of one or more vinyl monomers, for example styrene and acrylonitrile, in polymeric polyols, for example polyether polyols, or by the in situ reaction between a polyisocyanate and an amino- and/or hydroxyfunctional compound, such as triethanolamine, in a polymeric polyol.

15

Preferably, the polyol composition has an average hydroxyl equivalent weight of at least 1500. The average oxyethylene content of the polyol composition is preferably between 60 and 85% by weight.

20

Suitable low molecular weight chain extenders include aliphatic diols, such as ethylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 1,3-butanediol, 2,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, 2,2-dimethyl-1,3-propanediol, diethylene glycol, dipropylene glycol and tripropylene glycol, and aminoalcohols such as ethanolamine, N-methyldiethanolamine, N-ethyl-diethanolamine and the like. Ethylene glycol is preferred.

25

The amount of water is suitably less than 2% by weight, and preferably less than 1% by weight, based on the total weight of the isocyanate-reactive compounds.

30

In another aspect, the invention relates to microcellular elastomeric polyurethane foams having a density of less than 1000 kg/m³ and a Shore A hardness of at least 75. Preferably the density is less than 800 kg/m³ and the Shore A hardness at least 80. Most

preferably, the microcellular elastomeric polyurethane foams have a density of less than 600 kg/m³ and a Shore A hardness of at least 85.

In a further aspect, the invention provides a reaction system comprising:

- (i) a polyisocyanate containing at least 85% by weight of 4,4'-diphenylmethane diisocyanate or a variant thereof;
- (ii) a polyol composition comprising at least one polyoxyalkylene polyol containing oxyethylene residues, said polyol composition having an average nominal hydroxyl functionality of from 2 to 6, an average hydroxyl equivalent weight of at least 1300 and an average oxyethylene content of from 50 to 85% by weight,
- (iii) a chain extender having an average hydroxyl equivalent weight of from 15 to 250;
- (iv) water, and optionally,
- (v) one or more additives conventional to elastomer formulations.

This reaction system is used for making microcellular elastomeric polyurethane foams.

The term "reaction system" is defined as a system wherein the polyisocyanate is kept in a container separate from the isocyanate-reactive ingredients.

The isocyanate index of the reaction system, taking account of the polyol composition, water and any other isocyanate-reactive species, for example chain extenders or cross-linking agents, may be as low as 85 or as high as 120. Preferably, the isocyanate index is between 90 and 110.

The hardblock-content is preferably at least 50% by weight of the total composition.

Low molecular weight isocyanate-reactive compounds having an average functionality of 3 or more, such as glycerol, pentaerythritol or triethanolamine, may be added as crosslinking agents.

The foam-forming reaction mixture may contain one or more of the additives conventional to such reaction mixtures. Such additives include catalysts, for example tertiary amines and tin compounds, surface-active agents and foam stabilisers, for

example siloxane-oxyalkylene copolymers, flame retardants, organic and inorganic fillers, pigments, and internal mould release agents.

5 The process can be carried out according to the 'one-shot', 'semi-prepolymer' or 'prepolymer' method.

A wide range of elastomeric products can be made by the method of this invention.

10 The elastomers produced by the method of this invention can be used in a large variety of applications such as shoe soles and steering wheels.

The invention is illustrated by the following examples in which all parts, percentages and ratios are by weight.

15 The following glossary of materials is included to identify reaction components not otherwise identified in the examples.

Glossary

Polyisocyanate I: pure 4,4'-MDI (Suprasec MPR; Commercially available from ICI PLC; Suprasec is a trademark of ICI PLC).

Polyisocyanate II: uretonimine-modified MDI (Suprasec 2020; commercially available from ICI PLC; Suprasec is a trademark of ICI PLC).

Polyol A: Arcol 2580, a polyether triol having random oxyethylene and oxypropylene residues with a 76% oxyethylene content and OH-value of 42 mg KOH/g, commercially available from ARCO; ARCOL is a trademark of ARCO.

Polyol B: EO/PO triol having 10% EO-tip and OH-value of 36 mg KOH/g.

Polyol C: EO/PO diol having 75% random EO-groups and MW = 4000.

Catalyst: Dabco EG (33% solution of Dabco in EG obtainable from Air Products; Dabco is a trademark of Air Products).

EG: ethylene glycol.

DEG: diethylene glycol.

Examples 1-3 and comparative examples 1-4

Elastomers were moulded in a 15 x 10 x 1 cm mould in a conventional manner from the formulations given in the following Table.

Table 1

	EX. 1	EX. 2	EX. 3	Comp. EX. 1	Comp. EX. 2	Comp. EX. 3	Comp. EX. 4
5							
	POLYOL A	100	100	-	100	-	-
	POLYOL B	-	-	-	100	100	100
	POLYOL C	-	-	100	-	-	-
	EG	16.3	14	20	7.23	7.46	16.56
10	DEG	-	14	-	-	-	14.2
	CATALYST	0.5	0.5	0.7	1	1	0.5
	WATER	0.3	1	0.7	0.3	0.3	0.3
	POLYISOCYANATE I	Index 100	Index 100	-	Index 100	Index 100	Index 100
15	POLYISOCYANATE II	-	-	Index 100	-	-	-
	HARDBLOCK CONTENT (wt %)	50	50	57	35	35	50
	PROPERTIES						
20	DENSITY (kg/m ³)	702	536	420	650	651	crumbly material
	SHORE A HARDNESS	89	90	85	42	72	material
	ASKER C HARDNESS	93	90	89	66	82	no foam
	BALL REBOUND	36	26	N.M. ^(*)	64	57	foam

25

N.M.^(*): Not measured

30

These examples show that the use of polyols with a high oxyethylene content in high hardblock formulations results in elastomers having valuable properties which are processable up to high hardness, which is impossible or very difficult with formulations comprising polyols having a low oxyethylene content.

CLAIMS

1. A method for the preparation of microcellular elastomeric polyurethane foams from a reaction mixture comprising a polyisocyanate component, a polyol composition, a chain extender, water and optionally a cross-linking agent wherein the polyisocyanate component contains at least 85% by weight of 4,4'-diphenylmethane diisocyanate or a variant thereof, the polyol composition comprises at least one polyoxyalkylene polyol containing oxyethylene residues, said polyol composition having an average nominal hydroxyl functionality of from 2 to 6, an average hydroxyl equivalent weight of at least 1300 and an average oxyethylene content of between 50 and 85% by weight, and the chain extender has an average hydroxyl equivalent weight of from 15 to 250, the hardblock-content being more than 45% by weight.
2. A method according to claim 1 wherein the polyisocyanate component contains at least 90% by weight of 4,4'-diphenylmethane diisocyanate or a variant thereof.
3. A method according to claim 2 wherein the polyisocyanate component contains at least 95% by weight of 4,4'-diphenylmethane diisocyanate or a variant thereof.
4. A method according to any preceding claim wherein the polyoxyalkylene polyol containing oxyethylene residues is a poly(oxyethyleneoxypropylene) polyol.
5. A method according to any preceding claim wherein the polyol composition has an average nominal hydroxyl functionality of from 2 to 4.
6. A method according to any preceding claim wherein the polyol composition has an average hydroxyl equivalent weight of at least 1500.
7. A method according to any preceding claim wherein the polyol composition has an average oxyethylene content of 60 to 85% by weight.
8. A method according to any preceding claim wherein the hardblock-content is at least 50% by weight.

9. A method according to any preceding claim which is carried out at an isocyanate index of 90 to 110.
- 5 10. A microcellular polyurethane elastomeric foam having a density of less than 1000 kg/m³ and a Shore A hardness of at least 75.
11. A microcellular polyurethane elastomeric foam according to claim 10 having a density of less than 800 kg/m³ and a Shore A hardness of at least 80.
- 10 12. A microcellular polyurethane elastomeric foam according to claim 11 having a density of less than 600 kg/m³ and a Shore A hardness of at least 85.
13. A reaction system comprising:
- 15 (i) a polyisocyanate containing at least 85% by weight of 4,4'-diphenylmethane diisocyanate or a variant thereof;
- (ii) a polyol composition comprising at least one polyoxyalkylene polyol containing oxyethylene residues having an average nominal hydroxyl functionality of from 2 to 6, an average hydroxyl equivalent weight of at least 1300 and an average oxyethylene content of from 50 to 85% by weight;
- 20 (iii) a chain extender having an average hydroxyl equivalent weight of from 15 to 250;
- (iv) water, and optionally,
- (v) a cross-linking agent and one or more additives conventional to elastomer formulations.

INTERNATIONAL SEARCH REPORT

International Application No.
T/EP 97/02853A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/76 C08G18/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 547 765 A (ICI PLC) 23 June 1993 cited in the application see claims 1,3-6,8,9; table 2 ---	1-7,9-13
A	US 4 365 025 A (R.M.MURCH ET AL.) 21 December 1982 see column 8, line 34 - line 40; claims 1,17 --- -/--	1-3,13

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

2 October 1997

Date of mailing of the international search report

24.10.97

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INTERNATIONAL SEARCH REPORT

International Application No.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 106, no. 20, 18 May 1987 Columbus, Ohio, US; abstract no. 157765h, OGURO ET AL.: "water-resistant urethane-rubbers with high mechanical strength" page 67; column 1; XP002006847 see abstract & JP 61 238 816 A (ASAHI CHEMICAL) 24 October 1986 ---	1-5,7, 10-13
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Information on patent family members

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